

Document made available under the Patent Cooperation Treaty (PCT)

International application number: PCT/IL04/001110

International filing date: 07 December 2004 (07.12.2004)

Document type: Certified copy of priority document

Document details: Country/Office: US
Number: 60/621,014
Filing date: 22 October 2004 (22.10.2004)

Date of receipt at the International Bureau: 11 February 2005 (11.02.2005)

Remark: Priority document submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b)



World Intellectual Property Organization (WIPO) - Geneva, Switzerland
Organisation Mondiale de la Propriété Intellectuelle (OMPI) - Genève, Suisse

PCT/IL 2004 /001110

01 FEB 2005

PA 1271499

THE UNITED STATES OF AMERICA

TO ALL TO WHOM THESE PRESENTS SHALL COME:

UNITED STATES DEPARTMENT OF COMMERCE

United States Patent and Trademark Office

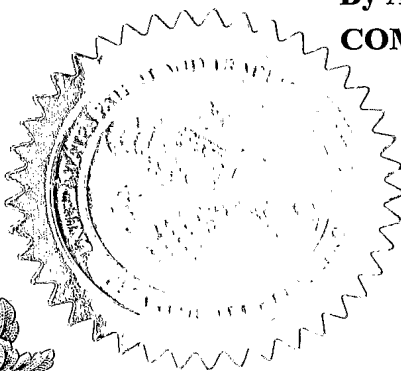
January 13, 2005

THIS IS TO CERTIFY THAT ANNEXED HERETO IS A TRUE COPY FROM THE RECORDS OF THE UNITED STATES PATENT AND TRADEMARK OFFICE OF THOSE PAPERS OF THE BELOW IDENTIFIED PATENT APPLICATION THAT MET THE REQUIREMENTS TO BE GRANTED A FILING DATE UNDER 35 USC 111.

APPLICATION NUMBER: 60/621,014

FILING DATE: *October 22, 2004*

By Authority of the
COMMISSIONER OF PATENTS AND TRADEMARKS



Lanai Jamison

LANAI JAMISON

Certifying Officer

18351 U.S. PTO
102204

PTO/SB/16 (08-03)

Approved for use through 07/31/2008. OMB 0651-0032

U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

PROVISIONAL APPLICATION FOR PATENT COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

Express Mail Label No. **EE 049927926 IL**

U.S. PTO
60/621014

102204

INVENTOR(S)				
Given Name (first and middle [if any])	Family Name or Surname	Residence (City and either State or Foreign Country)		
JACK L.	GILRON	BEER SHEVA, ISRAEL		
Additional inventors are being named on the _____ separately numbered sheets attached hereto				
TITLE OF THE INVENTION (500 characters max) INCREASING RECOVERY IN DESALINATION PROCESSES BY COMBINING REVERSE FLOW AND PRECIPITATION				
Direct all correspondence to: CORRESPONDENCE ADDRESS				
<input type="checkbox"/> Customer Number:	HA-REVAVA 2 BEER SHEVA 84225 ISRAEL			
OR				
<input type="checkbox"/> Firm or Individual Name				
Address				
Address				
City	State	Zip		
Country	Telephone	Fax		
ENCLOSED APPLICATION PARTS (check all that apply)				
<input checked="" type="checkbox"/> Specification Number of Pages	6	<input type="checkbox"/> CD(s), Number		
<input checked="" type="checkbox"/> Drawing(s) Number of Sheets	2	<input type="checkbox"/> Other (specify)		
<input type="checkbox"/> Application Date Sheet. See 37 CFR 1.76				
METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT				
<input checked="" type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27.	FILING FEE Amount (\$) \$80.00 xx			
<input checked="" type="checkbox"/> A check or money order is enclosed to cover the filing fees.				
<input type="checkbox"/> The Director is hereby authorized to charge filing fees or credit any overpayment to Deposit Account Number: _____				
<input type="checkbox"/> Payment by credit card. Form PTO-2038 is attached.				
The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.				
<input checked="" type="checkbox"/> No.				
<input type="checkbox"/> Yes, the name of the U.S. Government agency and the Government contract number are: _____				

[Page 1 of 2]

Respectfully submitted,
SIGNATURE Jack L. Gilron
TYPED or PRINTED NAME JACK L. GILRON
TELEPHONE +972-8-6461921 email: lgilron@bgu.ac.il

Date 19 OCT 2004
REGISTRATION NO. _____
(if appropriate)
Docket Number: _____

USE ONLY FOR FILING A PROVISIONAL APPLICATION FOR PATENT

This collection of information is required by 37 CFR 1.51. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 8 hours to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Mail Stop Provisional Application, Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

Title: Increasing recovery in desalination processes combining reverse flow and precipitation

Jack Gilron, Inventor

Description of invention:

This is a process designed to significantly increase recovery in desalination processes without excessive use of additional chemicals. It is intended for use with feeds of brackish water, treated wastewater, industrial water and seawater whenever there is a problem with sparingly soluble salts limiting recovery. The process as denoted in figure 1 involves three steps:

- a) a preconcentration step involving concentrating of ions of sparingly soluble salts by a membrane process (I) such as nanofiltration or reverse osmosis, which reject the multivalent ions of sparingly soluble salts which are mainly alkaline earth metals (Ca, Sr, Mg, Ba) and sulfate, in which this step is carried out under conditions of flow reversal allowing significant levels of supersaturation to be reached in the concentrate without attendant precipitation of the sparingly soluble salts on the preconcentration membrane. Flow reversal as outlined in US patent application US 60/529,668# involves changing the flow direction so that the feed is sent to the concentrate end of the series of membranes and the concentrate leaves from what was previously the feed end of the membrane series. As taught by U.S. application 60/529,668, by performing this flow reversal at intervals that are less than the induction period for crystallization at the membrane surface at the concentrate end of the membrane, no precipitation fouling occurs since the supersaturated solution is replaced by an undersaturated solution before it can occur. The flow reversal principle is illustrated in figure 2.

If the membrane process in step a) is nanofiltration and the salinity is still too high, the permeate can be sent to a further desalination process (III) such as a membrane process (reverse osmosis or electrodialysis) or a thermal process (e.g. multistage flash, multiple effect distillation, vapor compression distillation, membrane distillation) to generate a product water of requisite quality. This further desalination process can also be a combination of any of the processes mentioned here in order to increase recovery (for example reverse osmosis followed by a thermal evaporation process or electrodialysis).

If the membrane process in step a) is reverse osmosis the permeate usually can be used as desalination water as is.

- b) The supersaturated concentrate from the preconcentration step is sent to a vessel (II) containing a suspension of solids such as sand grains or calcium carbonate or calcium sulfate where precipitation occurs on these suspended solids which act as seeding surfaces. The excess concentration of supersaturated salts is released by precipitating on the seed surfaces. The solution which is now close to saturation is separated from the suspension by filtration on a microporous filter. Alternatively the supersaturated concentrate can be fed to the top (or bottom) of a fixed or moving bed of seed solids such

as is well known in the art of precipitation softening (lime or soda softening) and the softened solution is removed from the bottom (or top) of the bed after equilibrating to the equilibrium concentration of the sparingly soluble salts.

- c) The stream (4) from step b) - which is now nearly at equilibration with respect to sparingly soluble salts - is now fed back to the feed or an intermediate stage in the membrane process in step a). Alternatively it can be fed to an additional desalination step (membrane or thermal desalination) with a small amount of antiscalant, which now will be less given the smaller volume to be processed.

The advantage of this process is that the precipitation step (b) can take place without the addition of chemicals such as lime, caustic soda or sodium carbonate to generate supersaturation with respect to calcium. The solids formed on the seeds are more easily removed than in the case of the sludges formed in lime softening. The concentration that takes place in step a) already generates the supersaturation. An additional advantage to this process is that little or no antiscalant is needed since scaling is prevented in the preconcentration step by the reverse flow as taught in US application US 60/529,668. Therefore there is no antiscalant to interfere with the rate of precipitation in the precipitation step b).

Background and Introduction

Sparingly soluble salts can limit the recovery of desalination processes as their concentration increases in brine as more product water is pulled out of the feed stream. Different techniques have been used to cope with this problem. Chemical softening has been proposed to precipitate sparingly soluble salts most of which are salts of alkali earth metals (Ca, Sr, Mg, Ba). The problem with this approach is that it requires stoichiometric amounts of chemical to precipitate all of the metal ions of sparingly soluble salts. This is often a significant expense. For example, a brackish water containing 100 mg/L of calcium and 30 mg/L of magnesium, and 150 mg/L of carbonate alkalinity will require 185 g/m³ of hydrated lime and 135 g/m³ of soda ash to completely remove the calcium. At 80\$/ton for hydrated lime and 180\$/ton for soda ash this would involve a chemical cost of 2.5 cents/m³. In addition the sludges formed in lime softening are often voluminous and hard to remove. This can be prevented by using advanced precipitation processes that combine precipitation softening with microfiltration which has been denoted as membrane assisted crystallization (MAC) or filtering through a filter cake of calcium carbonate seeds which has been denoted as compact accelerated precipitation softening (CAPS).

Alternatively the pH can be reduced by adding acid and removing the carbonic acid formed by air stripping. This will eliminate the problem of carbonate scales but sulfate scales will still be a problem. For the example of brackish water mentioned in the previous paragraph, it would be necessary to add 120 g/m³ of sulfuric acid.

As a result the most common approach today is to use antiscalants which allow operation at various values of supersaturation. However even with the most advance antiscalants used today there are limits on the supersaturation levels, for example ~260-300% for calcium sulfate, an LSI index of 2.8 for calcium

carbonate and 200% for silica. This often means that recoveries are still often limited to 85-90%.

Another alternative is to use nanofiltration to remove the hardness ions. The permeate from the nanofilter can then be fed to reverse osmosis or thermal desalination units to recover the desalinated water at fairly high recoveries. However because counterions of the alkali earth metals are also rejected, supersaturation conditions are also reached in the nanofiltration step if the recoveries are high enough. Indeed it is important to reach high recoveries in the nanofiltration step because the overall recovery in two stages in series will be the product of the two steps. Therefore if recovery of the desalination step is 95% and the nanofiltration step is only 90%, then the overall recovery will be 85.5%. This is not much better than the recovery obtained in standard reverse osmosis (RO). One way of overcoming this is to recycle the concentrate of the desalination step to the nanofilter, but this raises the average salinity in the desalination step with attendant increase of salinity in the product.

To increase the recovery a number of researchers have proposed using precipitation softening on the concentrate before conducting further desalination on the treated concentrate. However this is complicated by the presence of antiscalants in the concentrate.

A previous application by the inventor, has outlined how flow reversal in nanofiltration (NF) or reverse osmosis (RO) can be used to prevent precipitation fouling of the membrane by sparingly soluble salts if the flow reversal (switching the feed and concentrate ends of the membrane train) is effected at a time less than the induction time for the given feed composition. Since the concentrate leaving such a flow reversal unit is already supersaturated, it can be fed to a seeded precipitator to relieve supersaturation by deposition on the seed crystals. The saturated solution leaving the precipitator can then be recycled to the reverse flow membrane unit for further water recovery.

Thus by incorporating a NF or RO unit with a seeded precipitator, one can significantly increase recovery without the need of large amounts of chemicals. Such a process is the claimed invention of this application. Depending on whether the flow reversal membrane unit is a reverse osmosis or a nanofiltration unit, the permeate can be used as product or sent to another desalination unit for further desalination. However because scaling ions have already been removed, the recoveries in the additional desalination unit can be much higher.

A Detailed Description of the Invention:

Please see the figure 1. The membrane preconcentration process is denoted by I, the seeded precipitation process is denoted by II, and the (optional) further desalination process is denoted by III. The feed stream (1) is fed to the membrane preconcentration process (I). This membrane preconcentration process constitutes either reverse osmosis (RO) which substantially retains all ions or nanofiltration (NF) which retains multivalent ions and partially passes monovalent ions. For nanofiltration, the rejections for the multivalent cations will usually be better than 80-90% and the rejection for sulfate will be better than 95%. For reverse osmosis the rejection of multivalent cations and sulfate will usually

exceed 99%. The membranes can be made from any of the accepted membrane materials- including but not limited to thin-film composite membranes made of polyamides or asymmetric membranes made from polyamide or cellulose acetate and its derivatives. The membrane elements can be spiral wound, plate and frame, tubular, or hollow fiber geometry provided that there is an arrangement to allow reversing the flow by switching the streams connected to the feed and reject fittings on the element. A preferred embodiment makes use of a spiral wound membrane elements.

The preconcentration unit is operated under a regime of flow reversal to prevent precipitation in the preconcentration step. An illustration of the principle of flow reversal is shown in figure 2. In figure 2a, a feed stream (21), whose concentration of sparingly soluble salt is less than that of the saturation concentration ($C_{21} < C_s$), is pressurized with a high pressure pump and the high pressure stream is fed to the left side (L) of a pressure vessel containing a series of one or more membrane elements (22). These membrane elements remove enough water through the membrane (M) into the permeate stream (23) that the exit stream (24) is concentrated in the retained sparingly soluble salts. The concentration of the sparingly soluble salts in the concentrate stream (24) is given by mass balance as :

$$C_{24} = \frac{Q_{21}C_{21} - Q_{23}C_{23}}{Q_{24}} \quad (\text{eq. 1})$$

where C refers to concentration (e.g. in g/L) and Q refers to volumetric flow rate (e.g. in L/hr). The subscript refers to the process stream to which the concentration and flow rate refers. Defining the recovery $Y = Q_{23}/Q_{21}$ as the portion of the feed stream (21) removed as permeate (23), one can rewrite equation 2 as:

$$C_{24} = \frac{C_{21} - YC_{23}}{(1 - Y)} \approx \frac{C_{21}}{(1 - Y)} \quad \text{when } C_{23} \ll C_{21} \quad (\text{eq 2})$$

If the recovery is high enough, then the sparingly soluble salt concentration at the membrane exit, C_{24} , can be greater than the saturation concentration (C_s) and the membrane elements at the right end (R) of the pressure vessel sees a supersaturated concentrate solution. Because of concentration polarization, the concentration of sparingly soluble salt at the membrane wall (C_w) will be always be greater than the concentration (C) in the bulk solution. Under conditions of supersaturation at the membrane surface, there will be an induction time τ_{wR} associated with the composition at the membrane wall next to the exit of the pressure vessel, C_{wR} . If the flow direction is then reversed (see figure 2b), then the membrane at the right end (R) of the pressure vessel (2) sees the feed which is at a concentration $C_{21} < C_s$ and the time accumulated in the induction period is lost, and will only begin again when the situation is returned to the one obtaining in figure 2a. Similarly under the conditions described in figure 2b, if recovery is high enough, then the concentration (C_{wL}) next to the membrane at the left end (L) of the pressure vessel which is now the exit, will exceed the saturation concentration ($C_{wL} > C_s$) and this will be associated with an induction time, τ_{wL} . When the flow is reversed and the situation reverts to that illustrated in figure 1a, the time accumulated in the induction period at the left end (L) of the pressure vessel is also lost, and the induction time at the right end (R) must again begin at 0. To generalize this picture, the description describes not only the very ends of the pressure vessel but also conditions obtaining further in, where supersaturations

can be still be reached. However the most extreme situations (and highest supersaturations) will usually be obtained at the ends.

This flow reversal can be effected as described in patent application US 60/529,668 previously submitted by the inventor of the present patent. Similarly in that patent, examples are given of successful demonstration of the technique.

Returning to the presently claimed process as described in figure 1, the concentrate stream (3) leaving unit (I) will normally have a supersaturation in excess of 200% in all sparingly soluble salts. If the feed is not acidified the feed will often have a langlier saturation index - $LSI > 2$ for calcium carbonate supersaturation. Stream (3) is fed to unit II which is a seeded crystallizer. This crystallizer can be in the form of a vessel containing the seeds kept in suspension by agitation, or a fluidized bed, or fixed bed. These crystallizers can take embodiments familiar to those versed in the art of precipitation lime softening - including but not limited to embodiments such as an upflow solid contactor clarifier (vessel with suspension) or a spiractor (fixed or fluidized bed contactor), and membrane aided crystallizers. A preferred embodiment will be given to those crystallizers in which the solids formed are compact and not voluminous as in the case of clarifiers. As such, packed and fluidized beds and membrane aided crystallizers will be preferred because of the ability to get a compact deposit for removal.

The seeds in the crystallizer can be seeds of the sparingly soluble salts (e.g. calcium carbonate or calcium sulfate) or fine sand (e.g. 0.1 – 2 mm in diameter – with sand often to be preferred in packed and fluidized beds). In the case of using seeds in an agitated suspension, a charge of 1- 10% (wt/vol) has been found effective in the case of calcium carbonate precipitation. Solids separation can be effected by gravity (in case of clarifiers, or packed or fluidized beds) or a membrane barrier. Where membranes are used to separate the near saturated water from the suspension of the crystallizer, any membrane can be used with pore sizes less than ~10 um if a filter cake of the crystalline solids is allowed to form on the membrane. If no filter cake is formed on the membrane, then it is preferred to use membranes with pore sizes of 0.2 micron or less. The membranes can be mounted in the crystallizer reaction tank and the treated fluid (4) removed by suction (as shown in the figure) or the membrane can be mounted on a side recycle stream, forcing the treated fluid (4) through the membrane under positive pressure.

The size of the crystallizer is dependent on the rate of sparingly soluble salt deposition on the seeds. The rate of deposition for sparingly soluble divalent salts is often given by an equation of the form:

$$\frac{dm}{dt} = S \cdot k(C - C_{sat})^n \quad (\text{eq 3})$$

Where dm/dt is the rate of salt precipitation per unit volume of reactor, S is the area of seeds per unit volume of the reactor, k is the rate constant for precipitation, C is the concentration of sparingly soluble salt and C_{sat} is the saturation concentration of the sparingly soluble salt. The exponent n , will usually be 2 for a reaction which is reaction limited and 1 for a reaction which is mass transport

limited. In any case it is clear that the more supersaturated the concentrate stream (3), C will be higher and the precipitation rate will be higher allowing a more compact crystallizer. By adding Alum to the crystallizer, it may be possible to coprecipitate silica as well. The solids or semi-solid slurry (5) are removed from the crystallizer according to methods known to those well versed in the art of precipitation/lime softening according to the choice of crystallizer equipment used and the solids or semi-solids (5) are then sent to disposal.

The treated fluid (4) which is at or slightly above saturation with respect to sparingly soluble salts is now returned to unit (I) where it is combined with the feed stream (1) or an intermediate stream within (I). Because it is near saturation and it is a much smaller volume than stream (1), the combined streams of (1) and (4) will usually not exceed saturation provided stream (1) is not saturated. In the event that (1) is near saturated or saturated, a small amount of antiscalant can be added to the combined streams of (1) and (4) to generate an induction time long enough to allow flow reversal to be effective. In such a case, because the amount of antiscalant is low (just enough to generate an induction time of 0.5 hours or more), it usually will not seriously impair the operation of the crystallizer (II) where there is a large concentration of seed crystals and supersaturation.

If an RO membrane or tight NF (NaCl rejection > 90%) is used in unit (I) then the product stream (2) can be often be used directly. If an open NF membrane is used in unit (I) then the product stream (2) is fed to another desalination unit (III) for further salt removal. Unit III can be any of the desalination processes known to those versed in the art of desalination and water treatment including membrane processes (NF, electrodialysis, reverse osmosis) or thermal desalination processes (for example, multiple effect distillation, multi-stage flash distillation, vapor compression distillation, membrane distillation). In this case, the product stream (6) is taken from unit III for use and the highly saline brine concentrate (7) is sent for disposal. It should be noted that very high recoveries are attainable in unit III because of the removal of scaling ions in the NF membrane process (I). Recoveries to be expected from unit III will exceed 50-60% when stream (1) is a seawater feed (>32,000 mg/L) and >90-95% when stream (1) is a brackish water feed (2000 - 8,000 mg/L).

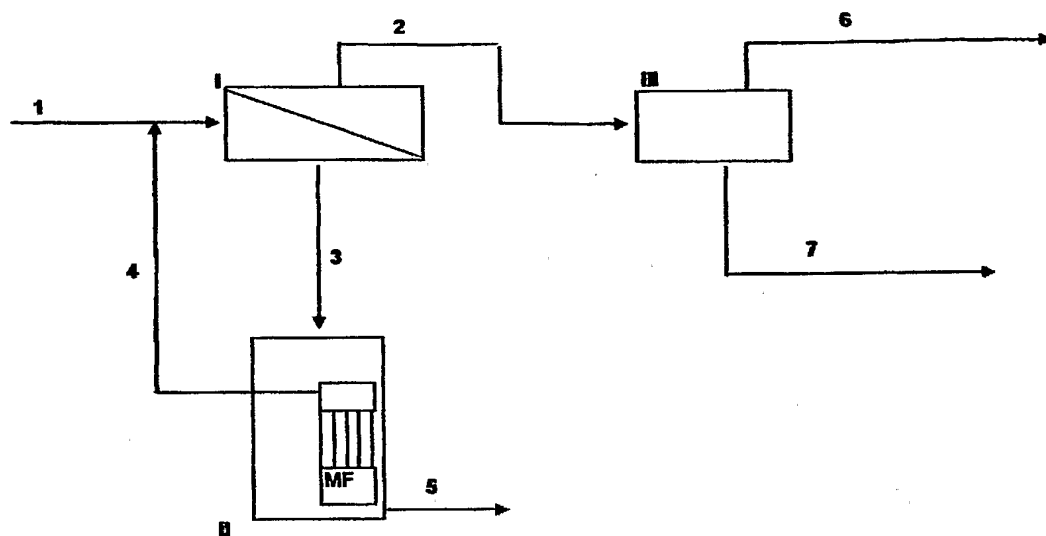


Figure 1: A schematic of the claimed process invention

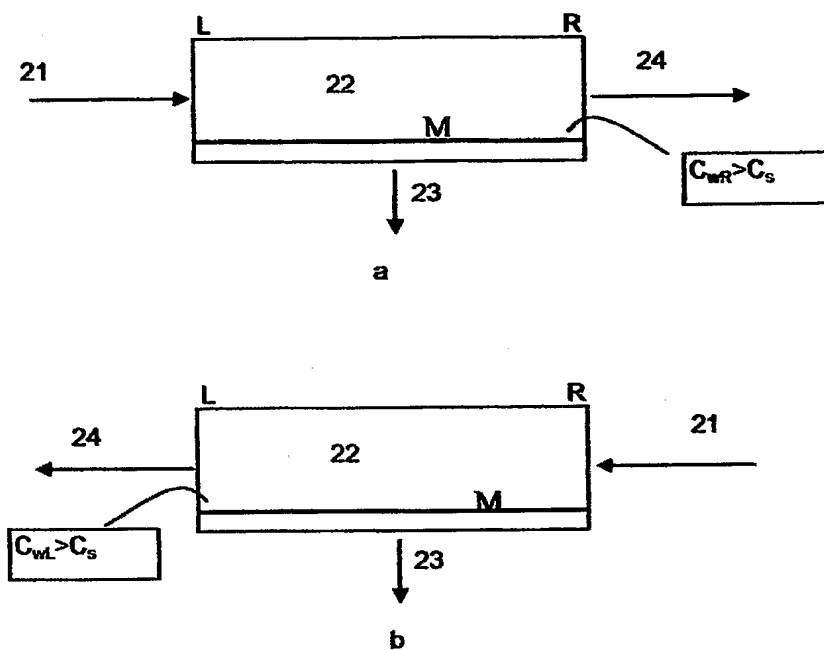


Figure 2: Flow reversal to prevent precipitation fouling, a) Flow direction under forward flow, b) Flow direction under flow reversal